

## **General Disclaimer**

### **One or more of the Following Statements may affect this Document**

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

X-621-68-407

PREPRINT

NASA TM X-63500

**A MASS SPECTROMETRIC TECHNIQUE  
FOR MEASUREMENT OF ATOMIC  
OXYGEN IN THE EARTH'S UPPER  
ATMOSPHERE**

**DAN N. HARPOLD  
CARL A. REBER**

**OCTOBER 1968**

**GSFC**

**GODDARD SPACE FLIGHT CENTER**  
**GREENBELT, MARYLAND**

**N 69-22158**

(ACCESSION NUMBER)		(THRU)	
32			
(PAGES)		(CODE)	
TMX 63500		13	
(NASA CR OR TMX OR AD NUMBER)			
(CATEGORY)			

PRECEDING PAGE BLANK NOT FILMED.

## ABSTRACT

Mass spectrometers carried on the Geoprobe rocket (NASA 8.25, Javelin) and Explorer 32 satellite were exposed to the atmosphere through knife-edged orifices. To facilitate the measurement of ambient atomic oxygen, the interior surfaces of the ion sources were coated with silver oxide to enhance surface recombination of the atomic species into molecular oxygen. At altitudes where there is no significant ambient molecular oxygen (>250 km), a determination of ambient atomic oxygen density is made by observing the density of molecular oxygen in the ion source and relating this density to the atomic species. If the recombination efficiency, determined at altitudes greater than 250 km, is independent of time, oxygen density, and other possible effects, the ambient molecular oxygen concentrations at lower altitudes can also be obtained from the measurement.

Data obtained from the Geoprobe and Explorer 32 experiments indicate: (1) the efficiency of surface recombination is considerably lower than anticipated; (2) the orificed-chamber technique yields good lower limits to the ambient abundance of atomic oxygen, as there is still uncertainty concerning adsorption or other loss mechanisms on the surfaces; (3) data obtained in the laboratory on surface effects of atomic oxygen at pressures above 0.1 torr apparently cannot be extrapolated to low pressures.

PRECEDING PAGE BLANK NOT FILMED.

CONTENTS

	<u>Page</u>
ABSTRACT . . . . .	iii
I. INTRODUCTION . . . . .	1
A. "Open" Ion Source . . . . .	1
B. Enclosed Ion Source . . . . .	4
II. MEASUREMENT OF ATOMIC OXYGEN BY RECOMBINATION . . . . .	7
A. Experimental Considerations . . . . .	7
B. Surface Preparation . . . . .	8
C. Laboratory Testing . . . . .	9
D. Flight Results . . . . .	12
III. CONCLUSIONS . . . . .	15
REFERENCES . . . . .	18

## ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Magnetic Mass Spectrometer Flown on the Explorer 17 Satellite . . . . .	21
2	Mass Spectrometer Flown on the Explorer 32 Satellite; Note Ion Source and Thermalization Chamber Which Encloses Ion Source . . . . .	22
3	System Used to Oxidize Ion Source and Chamber . . . . .	23
4a	Ion Current at Mass 44 From Time of Filament Activation; Uncoated Ion Source . . . . .	24
4b	Ion Current at Mass 44 with Silver Oxide Coated Ion Source . . . . .	25
5	Explorer 32 Satellite Showing One Mass Spectrometer Located on Spin Axis and One Mass Spectrometer Located on Spin Equator . . . . .	26
6a	Number Densities of Atomic and Molecular Oxygen Measured in the Ion Source of the Equatorial Spectrometer As a Function of Time From Exposure to the Atmosphere. Shown also are the Turn-On Numbers and the Angles-of-Attack, $\alpha$ , of the Instrument. . . . .	27
6b	Number Densities of Atomic and Molecular Oxygen Measured in the Ion Source of the Polar Spectrometer as a Function of Time From Exposure to the Atmosphere. Shown also are the Turn-On Numbers and the Angles-of-Attack, $\alpha$ , of the Instrument. . . . .	28
7	Ambient Atomic Oxygen Number Density as a Function of Altitude From Measurements Made on the Explorer 32 Satellite and the Geoprobe Rocket . . . . .	29

## I. INTRODUCTION

The measurement of atomic oxygen in the earth's upper atmosphere using mass spectrometric techniques is hampered by the extreme reactivity of the gas which creates two related experimental predicaments: (1) the difficulty in obtaining an accurate calibration in the laboratory and (2) the uncertainty in relating the number density in the mass spectrometer ion source to the number density in the ambient atmosphere. These difficulties and various experimental techniques for the measurement have been discussed extensively by Schaefer,<sup>1</sup> Nier,<sup>2</sup> Narcisi,<sup>3</sup> Reber,<sup>4</sup> and recently in review by von Zahn.<sup>5</sup> The purpose of this paper is to describe in some detail the technique used on the Explorer 32 satellite and Geoprobe rocket mass spectrometers in an attempt to reduce the uncertainty in this important measurement.

### A. "Open" Ion Source

Designing a mass spectrometer ion source which possesses a simple relationship between the measured quantity and the ambient atmosphere has, in general, proved to be quite formidable. It is in this area that most instrument development effort is presently being expended. Indeed, it is probably now true that the choice of analyzer (i.e., magnetic, quadrupole) is more a matter of vehicle and mission constraints than any real superiority of one type over another.

The earliest direct measurements of upper atmosphere composition by Townsend and Meadows<sup>6</sup> in 1957 using a Bennett radio frequency mass spectrometer gave indications of the difficulties to follow. Their data from three rocket flights covering an altitude range from 105 to 225 km exhibited a lower

$O/O_2$  ratio (4.4/1 at 225 km) than was anticipated, probably due to the recombination of atomic oxygen in the ion source and analyzer. Schaefer and Nichols<sup>1</sup> followed this in 1962 with their rocket quadrupole experiment between 100 and 190 km, using an ion source designed to be essentially insensitive to the gas-surface interactions. In this source, most of the neutral particles in the ionizing region should have experienced less than two collisions with a metal surface prior to entering the ionization region making it, in effect, nearly an "open" ion source. The relationship to the ambient atmosphere could then be expressed parametrically in terms of the thermal accommodation and recombination coefficients. In spite of some apparent difficulties in relating the output of the analyzer to the ambient atmosphere (as a function of vehicle orientation), this experiment yielded the highest  $O/O_2$  ratio, 10/1 at 190 km, measured up to that time.

A somewhat similar approach was used for the atmospheric composition experiment flown in 1963 on the Explorer 17 Aeronomy Satellite<sup>4</sup> (Fig. 1). Here the ion source was of the nearly open variety with the magnetically confined beam of ionizing electrons projecting outward from the satellite shell. The  $O/O_2$  ratio obtained from this experiment was effected by the attitude of the sensor and reached a maximum of 2.4/1 at angles-of-attack near 90 degrees, even though at the lowest altitude of measurement (250 km) the predicted ambient ratio is at least 15/1. Calculations showed that the major contribution to the density in the ion source came from particles which had entered the semi-enclosed volume behind the accelerator plate, experienced multiple collisions in the interior of the ion source, and were ionized while diffusing out through the electron beam. Thus it was concluded that the measured molecular oxygen came primarily from recombined atomic oxygen.

The exposed ion source approach has also been used by Nier and Hedin on a number of rocket flights with magnet analyzers.<sup>2,7</sup> These have yielded O/O<sub>2</sub> ratios of 16/1 for the 1963 flight<sup>2</sup> at 209 km and 3.84/1 for the 1965 flight<sup>7</sup> at 200 km. The difference in the two ratios has been attributed to both an increase in the O<sub>2</sub> measurement and a decrease in the O measurement on the 1965 flight.

The open ion source used on Explorer 17 has been refined, mated with a quadrupole mass analyzer, and flown on the Thermosphere Probe.<sup>8</sup> The major differences between this measurement and the satellite experiment include: improved venting of the ion source to reduce the gas flow back through the electron beam; improved focusing into the analyzer of the ions formed by electron bombardment; and lower vehicle velocity and consequently lower energy of the incoming neutral particles. By studying the response of the sensor at angles-of-attack near 90°, the effect of multiple bounce particles is greatly reduced. A rather sophisticated calculation, the results of which are dependent on gas-surface interactions, is again required to relate measured ion currents to atmospheric number densities.<sup>9</sup> It is not feasible at this time to apply the experience gained on this flight to a satellite experiment as the satellite velocities are four times those of the rocket, and the relative energies of the incoming particles are sixteen times those for the rocket measurement. Focussing of particles by the ion source at angles-of-attack near 90° is not nearly as efficient for these higher energies.

The attempt to "open up" the ion source to minimize gas-surface uncertainties creates another experimental difficulty: the large kinetic energy of the neutral gas particles (e.g., 10 ev for N<sub>2</sub> at satellite velocities) which is retained after ionization appears as an increase and/or a spread in the entrance angle and energy of the ions being injected into the analyzer. The variation in angle and energy is dependent on the angle-of-attack of the sensor, as well as the particle mass, and generally results in a variation in sensitivity of the experiment.

Since sufficient fluxes of neutral particles in the appropriate energy range are difficult to generate in the laboratory, these phenomena have not been investigated experimentally. Calculations and ray-tracing techniques indicate, however, that this variation in entrance angle and ion energy can have quite large effects under the conditions normally encountered during a rocket or satellite experiment. A satellite mass spectrometer utilizing an open ion source and requiring calculations, the results of which are dependent on gas-surface interactions, is thus subject to measurement uncertainties not only for atomic oxygen, but also for the inert gases such as helium and molecular nitrogen. The latter are unaffected by recombination but are sensitive to other interaction phenomena such as thermal accommodation and scattering mode (i.e., specular or diffuse).

#### B. Enclosed Ion Source

A well understood method of measuring inert gases from a rocket or satellite vehicle utilizes an ionization chamber exposed to the atmosphere through a knife-edged orifice. The particle density inside the chamber is related to the atmospheric density by the thermal transpiration equation modified for the velocity of the chamber, the so called F(S) equation:<sup>10,11</sup>

$$n_a = n_i \left( \frac{T_i}{T_a} \right)^{1/2} F(S) \quad (1)$$

where

$n_a$  = ambient particle number density

$n_i$  = measured density in ion source

$T_i$  = temperature of gage walls

$T_a$  = atmosphere temperature

$S = V \cos \alpha / V_p$

$V$  = vehicle velocity

$\alpha$  = angle between gage normal and velocity vector

$V_p$  = most probable velocity of atmospheric particles.

Experiments have been flown for several years using this technique to measure total atmospheric density and composition from rockets and satellites. Excellent consistency has been attained by experiments measuring the inert gases, in particular  $N_2$ , by many different experimenters; indeed, variations in results of measurements of  $N_2$  are now generally attributed to atmospheric differences, and not to inaccuracies in the measurement technique.

The Space Physics Research Laboratory at the University of Michigan, as part of a joint program with Goddard Space Flight Center, has flown a large number of chamber-enclosed omegatron mass spectrometers on rockets to measure  $N_2$  in the region between 120 and 350 km with very consistent results.<sup>8,12</sup> (Stated uncertainties are 10% relative and 25% absolute.) Recently this group flew a gold-plated mass spectrometer tuned to atomic oxygen, anticipating that this surface, with a low recombination coefficient for atomic oxygen, would reduce the probability of atomic oxygen recombination. An extremely low density for atomic oxygen was observed in flight (altitude range, 135 to 280 km) indicating that a relatively clean gold-plated surface is reactive in some way with atomic oxygen.<sup>13</sup>

Hedin and Nier,<sup>7</sup> at the University of Minnesota, flew a magnetic mass spectrometer with the ion source enclosed in a stainless steel chamber. This resulted in an almost complete loss of ambient atomic oxygen, while molecular nitrogen, molecular oxygen, helium and argon appeared to be unaffected by the steel surface.

Several enclosed ionization gauges have been flown on rockets and satellites measuring the neutral atmospheric pressure and density.<sup>14, 15, 16, 17</sup> The gauges were of two types - predominantly glass and predominantly stainless steel. Results from satellite experiments (perigee altitudes between 250 and 290 km) indicate no measurable pumping of atomic oxygen by either type of gauge.<sup>16</sup> There are two main differences between these measurements and those of the mass spectrometers using closed ion sources. First, the gauges were exposed to the ambient atmosphere for eight orbits (approximately twelve hours) before the satellite made useful measurements. Second, the gauges had been processed on the ground for a number of hours in an atmosphere of molecular oxygen at  $10^{-6}$  torr. Either of these conditions may have been sufficient to form an oxide layer on the interior surfaces of the gauges and thus inhibit further adsorption of atomic oxygen. In contrast, the total density measured by the glass gauges flown on the Geoprobe rocket<sup>16</sup> agreed with the molecular nitrogen number density measured by the neutral particle mass spectrometer (described below) flown on the same rocket and a simultaneous solar EUV extinction experiment. This indicated that atomic oxygen was not measured during the flight. In this case, the flight time was less than 30 minutes and the ionization gauges had not received the ground preparation in molecular oxygen that the satellite gauges had received.

## II. MEASUREMENT OF ATOMIC OXYGEN BY RECOMBINATION

### A. Experimental Considerations

It is clear that there are problems with either open or closed ion source geometries for measuring atomic oxygen. Since the closed geometry provides the most accurate data for the other atmospheric gases, it was decided to utilize this approach for measuring atomic oxygen as well by processing the interior surfaces to minimize loss of incoming atoms. Two possibilities were examined: (1) preparing the inner surfaces to minimize recombination and adsorption, and (2) preparing the surfaces so as to enhance recombination.

Calculations of the gas-dynamics of the enclosed ion source used on the mass spectrometer flown on the Explorer 32 satellite and the Geoprobe rocket indicate that incoming particles undergo at least fifty surface collisions on the average before entering the ionizing electron beam of the ion source. If the surface is such that  $\gamma$  is the probability of an atom being lost (recombined or adsorbed) per collision, the ratio of atoms remaining,  $n$ , to those entering,  $n_0$ , after  $N$  collision is

$$\frac{n}{n_0} = (1 - \gamma) (1 - \gamma) \dots = (1 - \gamma)^N. \quad (2)$$

$$\approx 1 - N\gamma. \quad (2a)$$

Thus, if  $N$  is greater than fifty it is desirable to have  $\gamma$  less than  $10^{-3}$  for all collisions if one wishes to make a 5% measurement by minimizing recombination and adsorption.

Since many surfaces in these ion sources could not be coated (e.g., the source magnet), any attempt to minimize the atomic oxygen interaction would still be affected in an unknown way by these surfaces. Conversely, enhancing recombination would greatly reduce the influence of the untreated surfaces by converting the "working gas" quickly into molecular oxygen. This approach then would significantly reduce the ambiguity in interpretation of high altitude data where the contribution to the measurement from ambient molecular oxygen would be small compared to the recombined atomic oxygen. Furthermore, it would eliminate the other major experimental difficulty, that of laboratory calibration in an atomic oxygen atmosphere; a straight forward calibration in a molecular oxygen atmosphere would be sufficient.

#### B. Surface Preparation

A number of investigators have studied the recombination properties of various surfaces.<sup>18,19,20,21</sup> Greaves and Linnett<sup>18</sup> obtained the highest value for the recombination coefficient on a metallic surface,  $\gamma = 2.4 \times 10^{-1}$ , for silver at 20°C. Greaves and Linnett<sup>18</sup> and Myerson<sup>19</sup> indicate that the high efficiency for recombination is probably due to the oxide layer which is built up following the initial exposure of metallic silver to atomic oxygen. To minimize the loss of atomic oxygen due to this chemical pumping during the early portion of the satellite flight (or during an entire rocket flight) the silver surfaces were exposed to atomic oxygen in the laboratory prior to flight.

The ion source (Figs. 1 and 2) was disassembled and the repeller, accelerator and lenses 1, 2 and 3 were electroplated with silver to a thickness of  $0.0076 \pm 0.0025$  mm. The interior surface of the chamber (Fig. 2) was

electroplated with silver to a thickness of  $0.051 \pm 0.025$  mm. The ion source was reassembled and the source and the chamber surface were separately exposed to atomic oxygen using the system shown in Fig. 3. Molecular oxygen was admitted to the system at a pressure of 0.5 to 1.0 torr. Atomic oxygen was produced in a plasma discharge maintained by a 2450 MHz microwave generator. The partially dissociated oxygen was passed through a small quartz leak to the region where the ion source was located; the pressure at the ion source was approximately  $10^{-2}$  torr. A liquid nitrogen cold trap was placed in series with the mechanical pump to prevent migration of pump oil back to the reaction region. No oxidation of the silver was observed after 20 minutes of exposure to the molecular oxygen. However, as soon as the microwave generator was turned on, the piece of silver immediately began to darken. The exposure of the silver to the atomic oxygen was continued until there was a fairly uniform oxide layer formed as indicated by a darkening of the surface.

During the period of experimentation with the flow system which preceded the final coating operation an interesting observation was made. The insertion of a small ( $\sim 3$  cm<sup>2</sup>) piece of silver coated material between the leak and the object to be oxidized increased by many orders of magnitude the time required to achieve a given degree of darkening of the object. The conclusion from this was that the atomic oxygen was being eliminated, though it was not possible to differentiate between adsorption on the silver or recombination.

### C. Laboratory Testing

To ascertain any potential difficulty in the interpretation of flight data (e.g. decomposition of the coating) a laboratory investigation was initiated on the silver

oxide surfaces. Analysis by X-ray diffraction indicated that the oxide consisted of approximately 70%  $\text{Ag}_2\text{O}$  and 30%  $\text{AgO}$ . Myerson<sup>19</sup> attributes the high catalytic efficiency of silver to the  $\text{Ag}_2\text{O}$  state of the oxide; he also calculates that  $\text{Ag}_2\text{O}$  is unstable at pressures below  $7\mu$ . To test this experimentally, a small sample of coated silver was stored at a pressure of  $10^{-8}$  torr for two weeks. At the end of this time the sample still possessed the characteristic dark gray coloration of the oxide. Subsequent analysis by X-Ray diffraction provided the same ratio of  $\text{Ag}_2\text{O}$  to  $\text{AgO}$  as in the original sample. Apparently the anticipated decomposition at low pressure is sufficiently slow that the relatively thick oxide coatings prepared on our system yield useful lifetimes for rocket and satellite experiments.

The second phase of the testing produced results which have not been satisfactorily explained. Since a normal step of the preparation of the flight sensors is a vacuum bake-out, samples of silver oxide metal were subjected to various temperatures to investigate their reaction to this environment. The results of this testing (some of which were obtained after the launch of the Explorer 32 satellite) are summarized below:

1.  $100^\circ\text{C}$  for 8 hours ( $P < 10^{-6}$  torr) - The characteristic dark gray color was unchanged. X-ray analysis indicated no  $\text{AgO}$  in sample; only  $\text{Ag}_2\text{O}$  remained. This is consistent with the higher decomposition vapor pressure of  $\text{AgO}$  ( $380\mu$  at  $20^\circ\text{C}$  compared to  $7\mu$  for  $\text{Ag}_2\text{O}$ ).
2.  $150^\circ\text{C}$  for 72 hours ( $P < 10^{-6}$  torr) - The dark gray color was unchanged. (No X-ray analysis was made at this time but the dark coloration generally coincides with the presence of  $\text{Ag}_2\text{O}$  as measured by the X-ray technique.)

3. 175°C for 36 hours ( $P < 10^{-6}$  torr) - The dark gray color had lightened noticeably. This apparently indicated the onset of loss of the oxide by decomposition.
4. 250°C for 24 hours ( $P < 10^{-5}$  torr) - The color of the surface changed to very light gray. X-ray analysis indicated no oxide remaining, only silver.

The results of the X-ray diffraction analysis of the surface heated to 250°C were not available until after the launch of Explorer 32. Prior to launch the response of this surface to atomic oxygen was investigated briefly. An uncoated sample of silver was placed downstream from the baked test surface in the coating system and exposed to a flow of atomic oxygen for a length of time sufficient to oxidize a much larger area. At the end of this time, neither the uncoated sample or the test surface had begun to discolor. It was concluded from this that the chemical (i.e. catalytic) properties of the surface had not been appreciably altered, but that the high temperature had modified some physical property such as the crystal structure. Of course, the later results of the X-ray analysis did not support this conclusion. Data from the rocket and satellite flights (discussed in the next section) however, indicate that the catalytic efficiency of this surface was not altogether impaired.

A comparison was then made of the background gas spectra of two mass spectrometers on the same vacuum system; these were identical except one had an uncoated ion source chamber and one had a coated and oxidized chamber.

Prior to the study the system was baked at 250°C for 24 hours. Background gases, with the exception of m/e 44, behaved similarly in both instruments, with the m/e 16 ion current being completely assignable to the dissociation of CO<sub>2</sub>, CO and O<sub>2</sub>. (The presence of CO<sub>2</sub> and O<sub>2</sub> in both instruments following bakeout is attributable to the ion pump used on this particular system; the background pressure was only in the 10<sup>-8</sup> torr region.) Figure 4 (a and b) shows the response of the instruments at m/e 44 when the filament is activated. The uncoated spectrometer exhibits a normal ion current vs. time profile when the filament is heated, going through a slight maximum at t = 4 seconds before stabilizing. The coated spectrometer exhibits two maxima, the usual one plus a secondary maximum at 7 seconds. There is apparently a secondary source of m/e 44 as the area near the filament heats up. Examination of the behavior of the fractionation peaks in the mass spectrometer (m/e 12, 14, 16, 22, 28, 30, 32) from m/e 44 yields no conclusive evidence to allow a choice between CO<sub>2</sub> and N<sub>2</sub>O as the source of this additional maximum.

#### D. Flight Results

The Geoprobe rocket (NASA 8.25) was launched at 1300 hrs. on 2 March 1966 and reached an altitude of 630 kilometers. The mass spectrometer was mounted with the orifice perpendicular to the rocket axis. The Explorer 32 satellite was launched on 25 May 1966 with two nearly identical spectrometers included in its complement of experiments, one on the spin axis and one on the spin equator (Fig. 5); atomic oxygen data were obtained from the perigee altitude of 287 km up to approximately 800 km. While detailed results from these flights are being prepared separately,<sup>22,23</sup> a brief account of the atomic oxygen data will be given here.

Figure 6 (a) and 6 (b) show the number densities of atomic and molecular oxygen measured in the ion source of the equatorial and polar mass spectrometers flown on the Explorer 32 satellite. The number densities are plotted as a function of time from initial exposure to the atmosphere and are indexed by turn-on number. The data shown were obtained between 288 and 318 km over a period of 115 hours. Included also in Fig. 6 (a) are the data from the Geoprobe rocket. The relative errors incurred in determining the values shown in Fig. 6 (a) and 6 (b) are approximately  $\pm 10\%$  for the satellite data and  $\pm 33\%$  for the rocket data; this is predominately reading error through telemetry and does not include errors associated with gas surface effects. At these altitudes the CIRA 1965 model atmosphere predicts the ambient molecular oxygen number density to be less than 5% that of atomic oxygen; the influence on these data of ambient molecular oxygen should then be quite small. It can be seen in Fig. 6 (a) that there is a tendency for the molecular oxygen number density to increase with time, while the atomic oxygen number density decreases. This effect suggests that a silver oxide layer, which enhances recombination (discussed in the previous section), builds up with time; hence, an increase in molecular oxygen and a decrease in atomic oxygen. Fig. 6 (b) shows the same quantities plotted for the polar spectrometer. Here the number density for atomic and molecular oxygen remain relatively constant with time. The difference in behavior between the two instruments is believed due to the neutral particles in the ion source of the equatorial spectrometer undergoing more internal wall collisions. Turn-on 59 exhibits lower molecular oxygen values and higher atomic oxygen values than the other turn-ons near the same time. The turn-on 59 values were obtained as the satellite was approaching perigee from apogee and thus had been at relatively low pressure for more than an hour; the other data were obtained either at perigee (turn-on 15) or a short time after perigee. The values for

turn-on 59 most likely indicate a pressure history effect on the surface recombination. Attitude of the sensors probably influences all the data as some angles of incidence produce more internal collisions than others; there is no correction for this effect in the data of Fig. 6(a) and Fig. 6(b), although the minimum angles-of-attack ( $\alpha$ ) are shown in the figures. Unfortunately, it was not possible to extend the duration of the measurement to see if the molecular and atomic oxygen trends shown in Fig. 6(a) and 6(b) stabilized, as electronic malfunctions terminated both experiments after the times shown.

The ambient atomic oxygen number density is obtained by summing the atomic and molecular species in the ion source and transforming by means of the thermal diffusion equation modified for vehicle velocity.

$$n_a(0) = n_{a1}(0) + n_{a2}(0) \quad (3)$$

where  $n_a(0)$  = ambient atomic oxygen number density

$$n_{a1}(0) = n_i(0) \left[ \frac{T_i}{T_a} \right]^{1/2} \frac{1}{F(S)} \quad (3a)$$

$$n_{a2}(0) = \sqrt{2} n_i(0) \left[ \frac{T_i}{T_a} \right]^{1/2} \frac{1}{F(S)} \quad (3b)$$

The factor  $\sqrt{2}$  in (3b) arises in calculating the effect of an atomic flux into and a molecular flux out of the chamber.

Results thus obtained from Explorer 32 and Geoprobe are shown in Fig. 7, plotted as a function of altitude; shown also is the CIRA 1965<sup>24</sup> model atmosphere

distribution of atomic oxygen for an exospheric temperature of 980°K. It can be seen that the data are in general lower by a factor of two or three than the model while the variation in density as a function of altitude is consistent with the model. The satellite data were obtained between 0800 hours and 1200 hours local time while the Geoprobe was flown near 1300 hours; the satellite turn-ons and the rocket flight were all mid-northern latitude. The differences in the densities determined from a given instrument are believed to be of atmospheric origin; this is borne out by the fact that the two instruments vary in the same way, within the limits of precision of the measurement.

The polar instrument gives higher densities by 40 to 100% than the equatorial spectrometer; this is most likely due to differences in the adsorption properties of the surfaces of the two instruments as a similar comparison for molecular nitrogen generally gives agreement to better than 10%. The lower absolute value for the measurement may indicate a too high value for the model density, or it may be the result of some loss mechanism which cannot be ascertained from the data available. It has been calculated that an adsorption probability of 0.01 would reduce the measured density to about 55% of the value for no adsorption, while an adsorption probability of 0.05 would cause a reduction to 25% of the value for no adsorption. However, the total mass density, obtained by summing the contributions of the major atmospheric constituents, agrees well with the mass density obtained from pressure gages on the same spacecraft.<sup>16</sup>

### III. CONCLUSIONS

It has generally been assumed that the most accurate measurements of atmospheric atomic oxygen using a mass spectrometer are obtained with an "open"

ion source. This technique presents difficulties in focusing the relatively high energy ions into the analyzer and in the interpretation of measurements of any atmospheric component. The high energy focusing problem is alleviated significantly on rocket vehicles; indeed, recent studies look very promising, using a nude ion source on a quadrupole analyzer. However, at the higher satellite velocities the problem still remains.

Mass spectrometers using enclosed ion sources, exposed to the atmosphere through knife-edged orifices, have been flown on a Geoprobe high altitude research rocket and on the Explorer 32 aeronomy satellite. The interior surfaces of the ion sources were specifically processed to enhance the recombination of atomic oxygen. Experience gained on these flights indicates:

1. forcing recombination in a closed ion source is a feasible technique for measurement of atomic oxygen at altitudes where molecular oxygen is negligible;
2. recombination coefficients measured in the laboratory at higher pressures are not consistent with the data acquired at high altitudes and pressures less than  $10^{-5}$  torr;
3. values obtained for ambient atomic oxygen number densities are good lower limits due to uncertainties concerning loss processes.

If loss mechanisms can be neglected, a precise knowledge of the recombination coefficient is not required to make meaningful measurements of atomic oxygen in

regions where molecular oxygen is a minor component. However, for lower altitudes, a precise measurement of ambient O requires a constant value of the recombination coefficient. It is not clear from the data from these two flights if this parameter stabilizes at the higher values of atomic oxygen density or whether it continues to increase.

There is a clear need for better information on the behavior of atomic oxygen on surfaces at pressures less than  $10^{-5}$  torr, regarding both recombination and adsorption effects. This information, when it becomes available, will enable a significant improvement in the study of one of the most important constituents of the earth's upper atmosphere.

## REFERENCES

1. E.J. Schaefer, and M.H. Nichols, *J. Geophys. Res.*, 69, 4649-4660, (1964).
2. A.O. Nier, J.H. Hoffman, C.Y. Johnson, and J.C. Holmes, *J. Geophys. Res.*, 69, 979-989, (1964a).
3. R.S. Narcisi, H.I. Schiff, J.E. Morgan, and H.A. Cohen, AFCRL Instrumentation Paper No. 42.
4. C.A. Reber, *Planet. Space Sci.*, 13, 617-646, (1965).
5. U. von Zahn, *J. Geophys. Res.*, 72, 5933-5937, (1967).
6. E.B. Meadows, and J.W. Townsend, Jr., *Space Res.* 1, 175-198, (1960).
7. A.E. Hedin, and A.O. Nier, *J. Geophys. Res.*, 71, 4121-4131, (1966).
8. D.R. Taeusch, and G.R. Carignan, University of Michigan Scientific Report No. 07065-5-R, (1967).
9. H.B. Niemann, and J.R. Krick, University of Michigan Scientific Report No. 07065-3-S (1966).
10. F.V. Schultz, N.W. Spencer, and A. Riefman, Upper Air Research Program Report No. 2, Engineering Research Institute, University of Michigan (1948).
11. R. Horowitz, and H.E. LaGow, *J. Geophys. Res.*, 62, 57-77, (1957).

12. N.W. Spencer, L.H. Brace, G.R. Carignan, D.R. Tausch, and H. Nieman, *J. Geophys. Res.*, 70, 2665-2698, (1965).
13. G.R. Carignan, private communication.
14. N.W. Spencer, R.L. Boggess, H.E. LaGow and R. Horowitz, *Am. Rocket Soc. Journal* 29, 290, (1959).
15. G.P. Newton, R. Horowitz, and W. Priester, *Planet. Space Sci.*, 13, 599-616, (1965).
16. D.T. Pelz, and G.P. Newton, Paper presented at 49th meeting Am. Geophy. Union, Washington (1968).
17. G.P. Newton, and D.T. Pelz, Paper presented at 49th meeting of Am. Geophy. Union, Washington (1968).
18. J.C. Greaves, and J.W. Linnett, *Trans. Faraday Soc.*, 54, 1323-1330, (1958).
19. A.L. Myerson, *J. Chem. Phys.*, 38, 2043-2045, (1963).
20. B.J. Wood, and H. Wise, *Rarefied Gas Dynamics*, Supplement 1, 55-59, (1961).
21. J.W. Linnett, and D.G.H. Marsden, *Proc. Royal Soc.*, 234, 504-515, (1956).

22. C.A. Reber, A.E. Hedin, J.E. Cooley, and D.N. Harpold, to be published.
23. J.E. Cooley, and C.A. Reber, to be published.
24. CIRA 1965, COSPAR International Reference Atmosphere 1965, North Holland Publishing Company, Amsterdam, (1965).

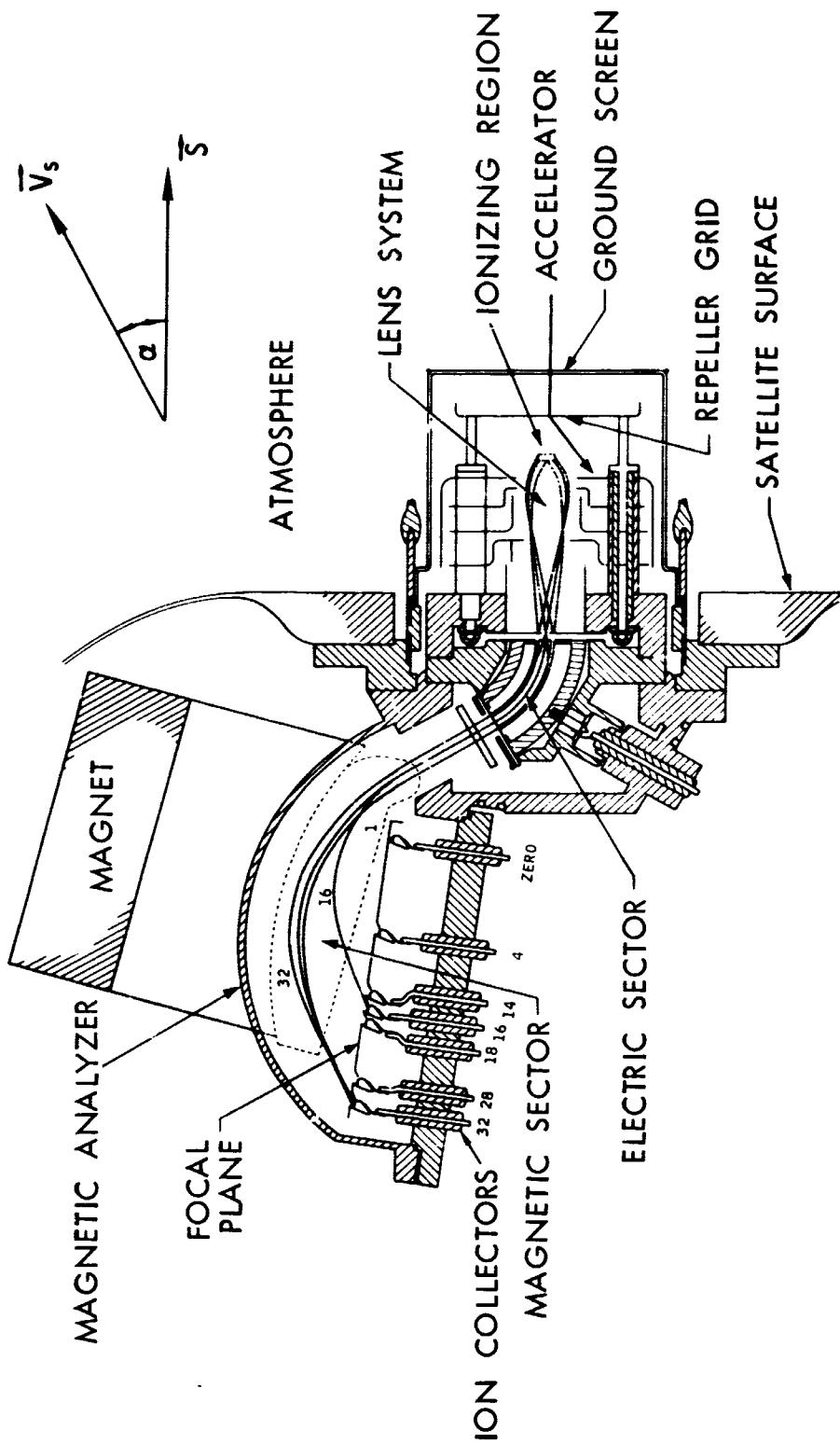


Figure 1. Magnetic Mass Spectrometer Flown on the Explorer 17 Satellite

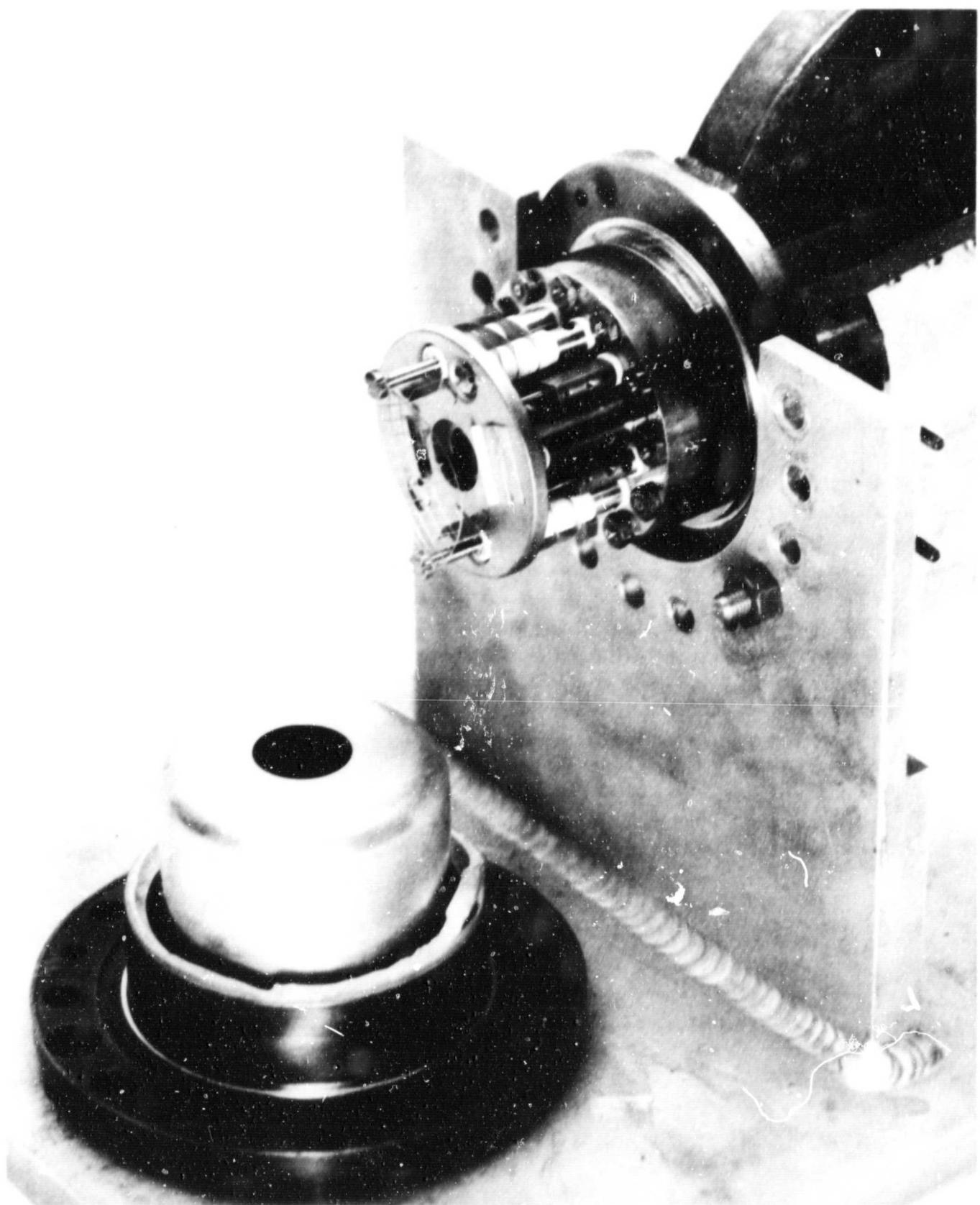


Figure 2. Mass Spectrometer Flown on the Explorer 32 Satellite; Note Ion Source and Thermalization Chamber Which Encloses Ion Source

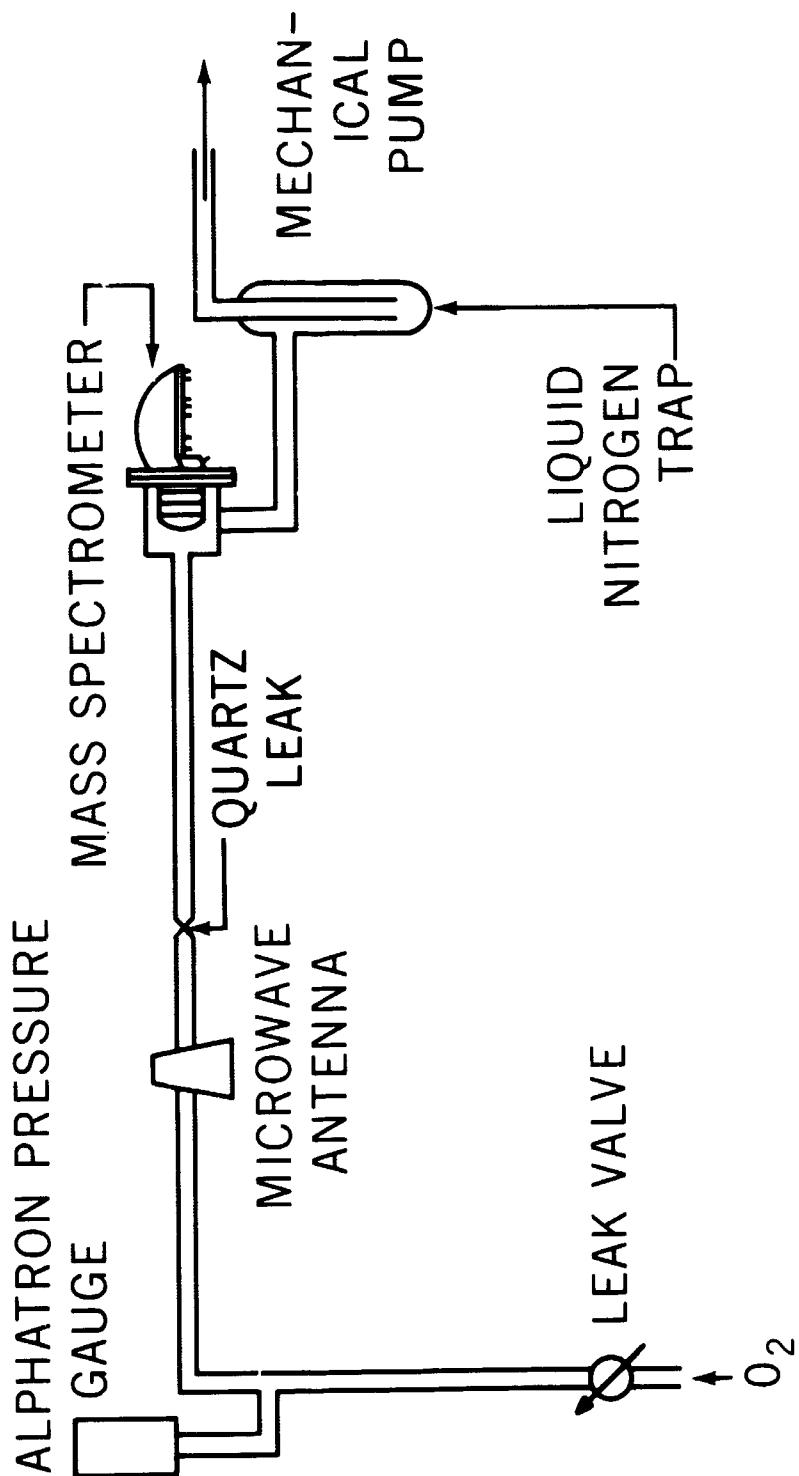


Figure 3. System Used to Oxidize Ion Source and Chamber

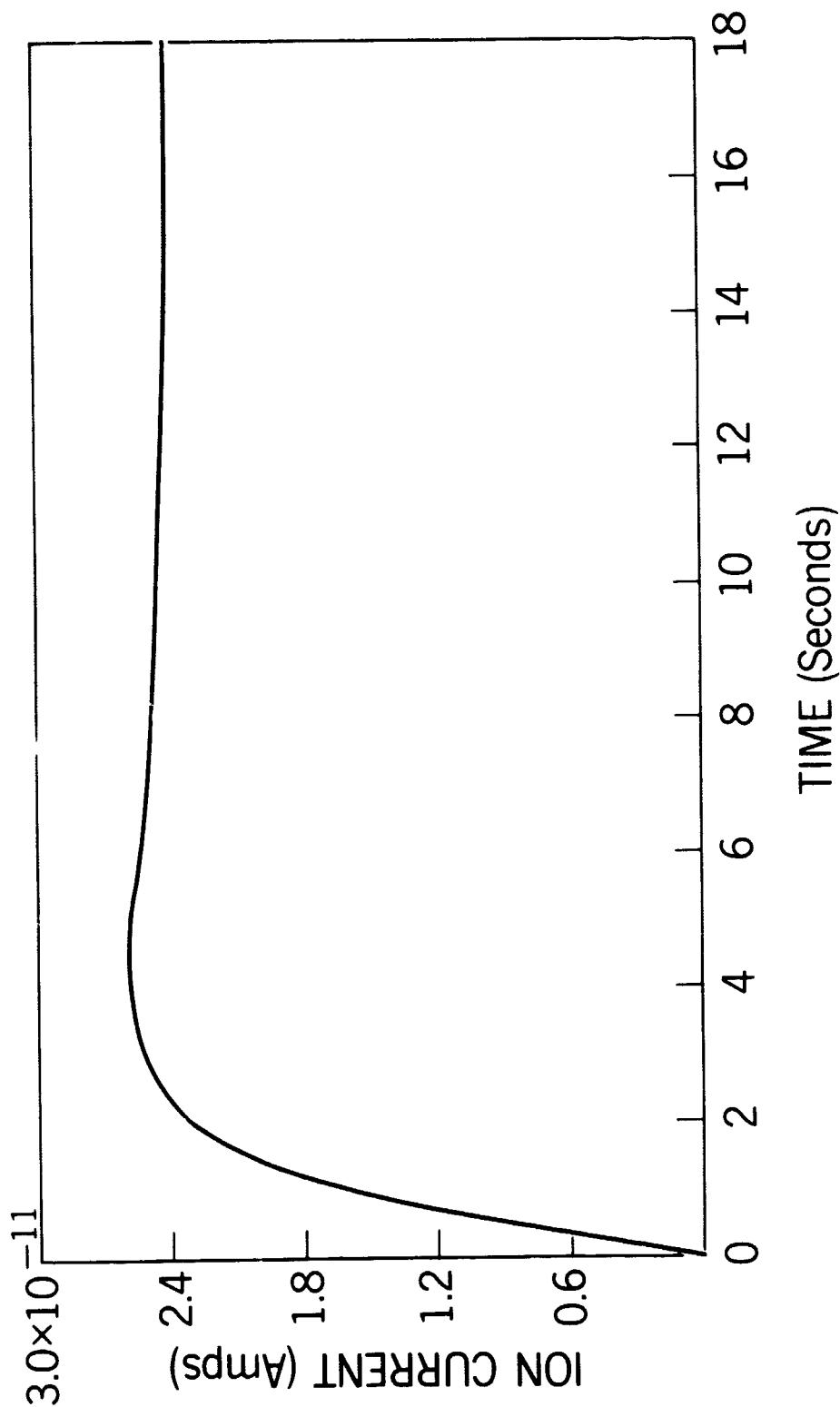


Figure 4a. Ion Current at Mass 44 From Time of Filament Activation; Uncoated Ion Source

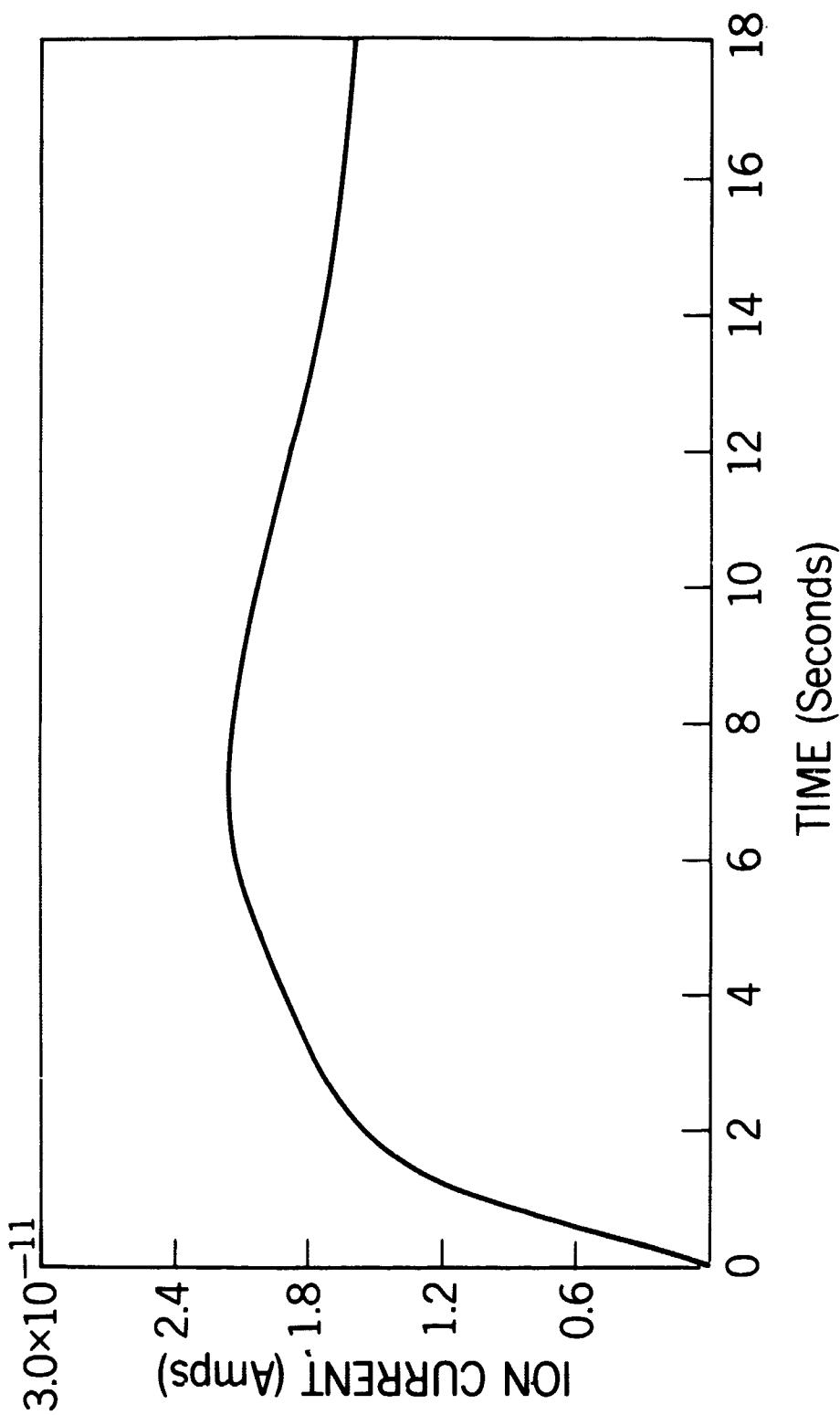


Figure 4b. Ion Current at Mass 44 With Silver Oxide Coated Ion Source

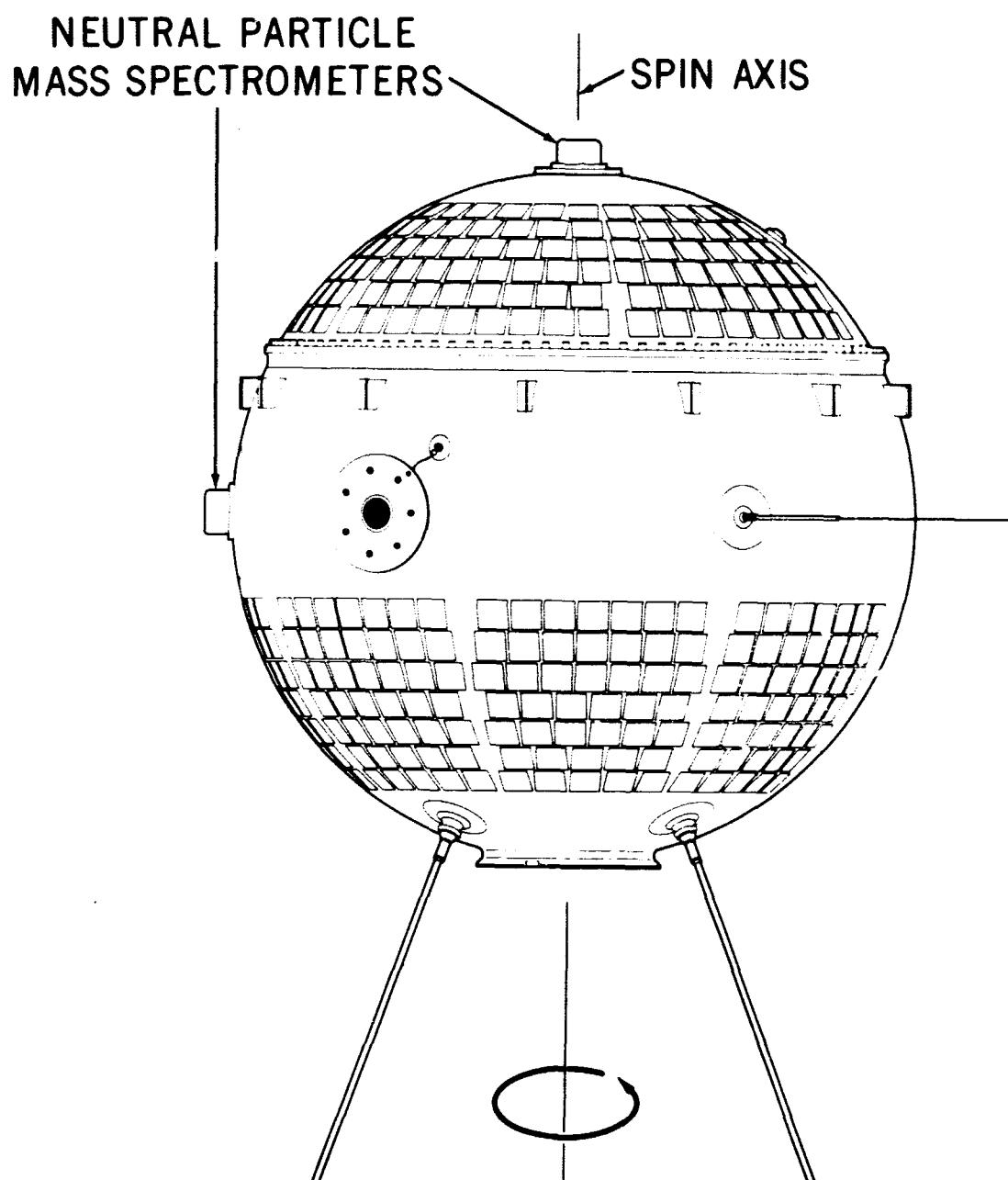


Figure 5. Explorer 32 Satellite Showing One Mass Spectrometer Located On Spin Axis and One Mass Spectrometer Located on Spin Equator

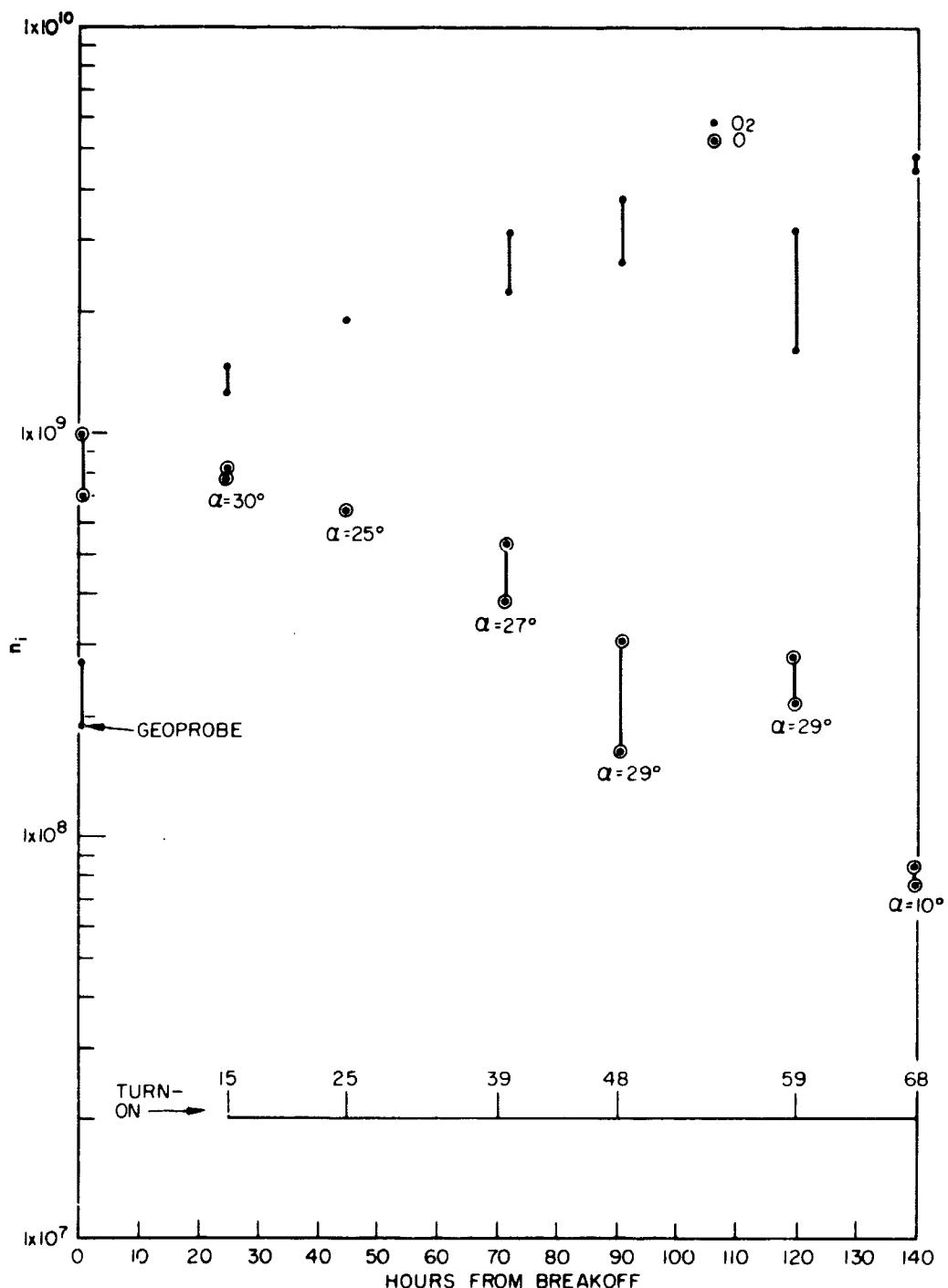


Figure 6a. Number Densities of Atomic and Molecular Oxygen Measured In the Ion Source of the Equatorial Spectrometer as a Function of Time From Exposure to the Atmosphere. Shown also are the Turn-On Numbers and the Angles-of-Attack,  $a$ , of the Instrument.

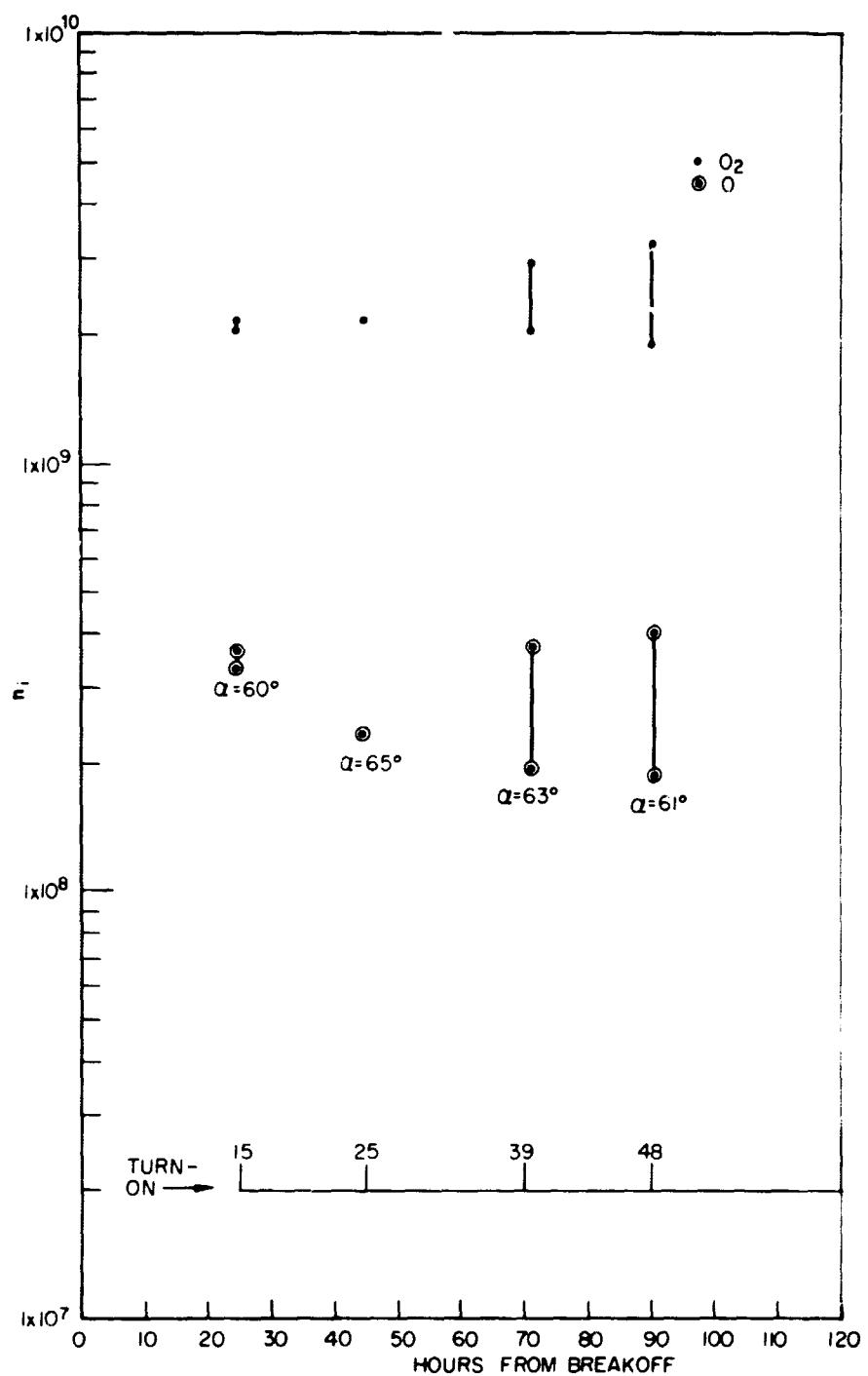


Figure 6b. Number Densities of Atomic and Molecular Oxygen Measured in the Ion Source of the Polar Spectrometer as a Function of Time From Exposure to the Atmosphere. Shown also are the Turn-On Numbers and the Angles-of-Attack,  $\alpha$ , of the Instrument.

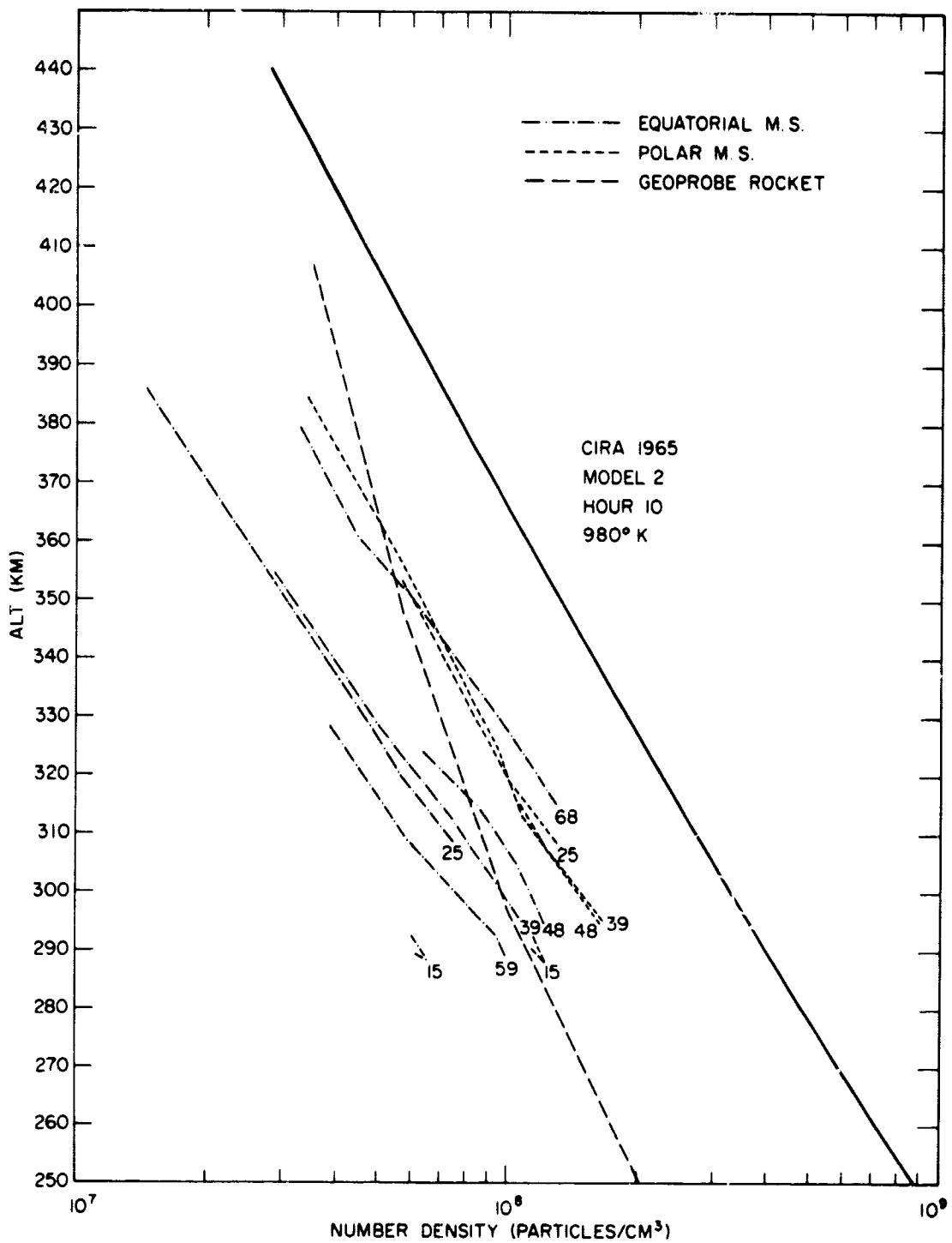


Figure 7. Ambient Atomic Oxygen Number Density as a Function of Altitude From Measurements Made on the Explorer 32 Satellite and the Geoprobe Rocket